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L5: Entry 1 of 1 File: USPT Aug 28, 2001

DOCUMENT-IDENTIFIER: US 6281307 B1
TITLE: Polymerizable composition, process for producing cross linked polymers, and cross-linkable polymers

Abstract Text (1):
Composition comprising (a) catalytic amounts of a one-component catalyst for metathesis polymerization and (b) at least one polymer with strained cycloalkenylene radicals bonded in the polymer backbone, alone or as a mixture with strained cycloolefins. The composition can be polymerized thermally or photochemically by metathesis polymerization and is suitable for the production of shaped articles, coatings and relief images. The catalyst is selected from Ruthenium and Osmium compounds.

Brief Summary Text (1):
The present invention relates to a composition of unsaturated polymers, in the polymer backbone of which is bonded a strained cycloalkenylene, with a one-component catalyst for metathesis polymerization which is induced thermally or by actinic radiation; a process for the polymerization of the composition; materials coated with the composition or the polymerized composition, and shaped articles of the crosslinked polymers; and crosslinkable polymers.

Brief Summary Text (2):
Thermally induced ring-opening metathesis polymerization using catalytic amounts of metal catalysts has already been known for a relatively long time and described in many cases in the literature [see, for example, Ivin, K. J., Olefin Metathesis 1-12, Academic Press, London (1983)]. Polymers obtainable in this way are prepared industrially and are commercially obtainable, for example under the trade name Vestenamer.RTM.. The industrial preparation is carried out using highly reactive two-component catalysts, as a rule transition metal halides, for example WCl.sub.6 and metal-alkylenes, for example zinc-, aluminium- or tin-alkylene. The polymerization or gelling starts immediately after a cycloolefin has been combined with the two catalyst components. The mixtures of cycloolefin and catalyst therefore have exceptionally short pot lives, and they are suitable in practice only in the reaction injection moulding process (RIM process). The severe heating of the reaction mixture due to the heat of reaction, which imposes very high technical requirements on a controlled reaction temperature, is also a disadvantage. It is therefore difficult to adhere to a polymer specification. WO 93/13171 describes air- and water-stable one-component and two-component catalysts based on molybdenum and tungsten compounds containing carbonyl groups and ruthenium and osmium compounds having at least one polyene ligand for thermal metathesis polymerization and a photoactivated metathesis polymerization of strained cycloolefins, in particular norbornene. No other polycyclic--above all non-fused polycyclic--cycloolefins are mentioned. The one-component catalysts of the ruthenium compounds used, that is to say [Ru(cumene)Cl.sub.2].sub.2 and [(C.sub.6 H.sub.6)Ru(CH.sub.3 CN).sub.2 Cl].sup.30 PF.sub.6.sup.-, can indeed be activated by UV irradiation; however, the storage stability of the compositions with norbornene are [sic] completely unsatisfactory. These catalysts can replace the known two-component catalysts only in adequately. Demonceau et al. [Demonceau, A., Noels, A.

F., Saive, E., Hubert, A. J., J. Mol. Catal. 76: 123-132 (1992)] describe (p-cumene)RuCl.sub.2 P(C.sub.6 H.sub.11).sub.3, (C.sub.6 H.sub.5).sub.3].sub.3 PRuCl.sub.2 and (C.sub.6 H.sub.5).sub.3].sub.3 PRuHCl as thermal catalysts for the ring-opening metathesis polymerization of norbornene, a fused polycycloolefin. Because their activity is too low, these catalysts have not found acceptance in industrial preparation. It is therefore proposed to increase the activity by the addition of diazoesters. It is also mentioned that only (p-cumene)RuCl.sub.2 P (C.sub.6 H.sub.11).sub.3 is capable of polymerizing norbornene in a relatively short time at 60.degree. C. Cyclooctene is also mentioned as a further monomer. No other cycloolefins are mentioned for the methatesis [sic] polymerization.

Brief Summary Text (3):
Petasis and Fu [Petasis, N. A., Fu, D., J. Am. Chem. Soc. 115: 7208-7214 (1993)] describe the thermal ring-opening metathesis polymerization of norbornene using bis-cyclopentadienyl-bis(trimethylsilyl)methyl-titanium(IV) as a thermally active catalyst. No other cycloolefins are mentioned for the metathesis polymerization.

Brief Summary Text (6):
The invention first relates to a composition comprising (a) catalytic amounts of a one-component catalyst for metathesis polymerization and (b) at least one polymer with strained cycloalkenylene radicals bonded in the polymer backbone, alone or mixed with strained cycloolefins.

Brief Summary Text (21):
It is known to the expert that cyclohexene can be polymerized by metathesis only with difficulty or not at all. Cyclohexene radicals of the formula (a) are therefore not preferred. Structural units of the formula (a) in which R.sub.01 and R.sub.02 together do not form a double bond are preferred.

Brief Summary Text (49):
The polyamides are preferably linear and accessible either by or transamidation processes on the corresponding monomers, or by Diels-Alder reaction of polyamides with olefinically unsaturated dicarboxylic acid and/or diamine structural units with open-chain or preferably cyclic 1,3-dienes to form strained cycloolefin rings. Mono-, di- or tricyclic dienes are preferably used for the Diels-Alder reaction.

Brief Summary Text (66):
One embodiment can be essentially or completely linear metathesis polymers of fused at least bicyclic cycloaliphatic dienes which contain two olefinic double bonds in different rings. The individual rings can contain 3 to 12, preferably 5 to 8 ring C atoms. The polymers contain, for example, recurring structural elements of the formula (r)

Brief Summary Text (98):
In another embodiment, the polymers with a carbon backbone are metathesis polymers of strained cycloolefins with a double bond in the ring, or copolymeric metathesis polymers of strained cycloolefins with a double bond in the ring and olefinically unsaturated comonomers, of which the olefinic double bonds in the polymer backbone are reacted partly or completely with open-chain or cyclic 1,3-dienes having 4 to 12, preferably 5 to 8 C atoms in a Diels-Alder reaction to give cycloalkenylene radicals having 6 to 14, preferably 7 to 12 C atoms. Preferably 5 to 80%, more preferably 5 to 60%, and in particular 10 to 50% of the double bonds are reacted.

Brief Summary Text (99):
In a preferred embodiment, these metathesis polymers contain recurring structural elements of the formula (t) ##STR7##

Brief Summary Text (102):
In another preferred embodiment, the metathesis polymer contains recurring structural units of the formula (u) ##STR9##

Brief Summary Text (106):
These metathesis polymers are novel and the invention likewise relates to them.

Brief Summary Text (116):
The processes for the preparation of the abovementioned polymers are known or analogous to known processes. The starting monomers and polymers are likewise known and are in some cases commercially obtainable or can be prepared by analogous processes. Diels-Alder reactions are advantageously carried out in solvents and expediently under increased pressure. Metathesis copolymers and processes for their preparation are described, for example, in U.S. Pat. No. 5,215,798. These polymers or metathesis polymers of strained cycloolefins can also be prepared with the catalysts described below. Diels-Alder reactions can be carried out analogously to the process described in EP 287 762.

Brief Summary Text (117):
The choice of the polymers to be used according to the invention depends chiefly on the intended use and the desired properties. The wide selection by modifications of the polymers allows tailor-made polymers to be provided for the most diverse uses. A further modification possibility results from the concomitant use of strained cycloolefins which are capable of metathesis polymerization, which means that, overall, adaptations specific to desired uses can be carried out.

Brief Summary Text (256):
Suitable inert solvents are, for example, protic-polar and aprotic solvents, which can be used alone or in mixtures of at least two solvents. Examples are: ethers (dibutyl ether, tetrahydrofuran, dioxane, ethylene glycol monomethyl or dimethyl ether, ethylene glycol monoethyl or diethyl ether, diethylene glycol diethyl ether and triethylene glycol dimethyl ether), halogenated hydrocarbons (methylene chloride, chloroform, 1,2-dichlorethane, 1,1,1-trichlorethane and 1,1,2,2-tetrachlorethane), carboxylic acid esters and lactones (ethyl acetate, methyl propionate, ethyl benzoate, 2-methoxyethyl acetate, .gamma.-butyrolactone, .delta.-valerolactone and pivalolactone), carboxylic acid amides and lactams (N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, tetramethylurea, hexamethylphosphoric acid triamide, .gamma.-butyrolactam, .epsilon.-caprolactam, N-methylpyrrolidone, N-acetylpyrrolidone and N-methylcaprolactam), sulfoxides (dimethyl sulfoxide), sulfones (dimethyl sulfone, diethyl sulfone, trimethylene sulfone and tetramethylene sulfone), tertiary amines (N-methylpiperidine and N-methylmorpholine), aliphatic and aromatic hydrocarbons, for example petroleum ether, pentane, hexane, cyclohexane, methylcyclohexane, benzene or substituted benzenes (chlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene, nitrobenzene, toluene and xylene) and nitriles (acetonitrile, propionitrile, benzonitrile and phenylacetonitrile). Preferred solvents are aprotic polar and non-polar solvents.

Brief Summary Text (265):
Heat stability in the context of the invention means that the photocatalytically active metal compounds form no active species for the ring-opening metathesis polymerization when heated. For example, at room temperature to slightly elevated temperature, such as about +40.degree. C., the catalyst can initiate no ring-opening metathesis polymerization with exclusion of light in the course of weeks. Only an insignificant amount (less than 0.2% by weight) of monomer is reacted during this period. The heat stability can be determined, for example, by storing a toluene solution with 20% by weight of monomer and 0.33% by weight of metal catalyst in the dark at 50.degree. C. for 96 hours, and any amount of polymer formed, which can be detected by the build-up in viscosity and can be determined quantitatively by precipitation in a precipitant, for example ethanol, filtration and drying, is not more than 0.5% by weight, and preferably not more than 0.2% by weight.

Brief Summary Text (267):

Photolabile ligand in the context of the present invention means that when the catalyst is irradiated by light in the visible or ultraviolet spectral range, the ligand dissociates from the catalyst and forms a catalytically active species for the metathesis polymerization. Nonionic photolabile ligands are preferred according to the invention.

Brief Summary Text (527):
Sterically bulky substituents in the context of the invention are understood as meaning those which shield the ruthenium and osmium atoms sterically. It has thus been found, surprisingly, that linear alkyl groups as substituents in the phosphine and phosphite ligands result in ruthenium compounds without any thermal activity for the metathesis polymerization of strained cycloolefins. It has also been observed that in the case of osmium compounds, surprisingly, linear alkyl groups as substituents in the phosphine and phosphite ligands have an excellent thermocatalytic activity for the metathesis polymerization of strained cycloolefins; however, phosphine and phosphite ligands with sterically bulky substituents are also preferably used for the osmium compounds. It has furthermore been found that the steric shielding of triphenylphosphine ligands in ruthenium dihalides and ruthenium hydride-halides is inadequate, and such catalysts have only a moderate catalytic activity for the metathesis polymerization of strained cycloolefins. The catalytic activity can suprisingly be increased considerably if the tertiary phosphine groups contain phenyl substituted by alkyl or alkoxy groups.

Brief Summary Text (549):
The compositions according to the invention are surprisingly stable to storage and can be marketed as such. However, it is also possible to mix the individual components together before processing. If air- and/or moisture-sensitive catalysts are used, storage with exclusion of air and moisture is advisable. Since the novel crosslinking principle is not based on a free radical, anionic or cationic reaction, practically no interruption or slowing of the reaction is observed on carrying out the polymerization in air, which offers considerable advantages during processing, for example no extensive protective precautions. The possibility of using solyent-free systems in the case of liquid polymers of low molecular weight or in the case of solutions with reactive strained cycloolefins which are capable of metathesis polymerization as comonomers is a great surprising advantage.

Brief Summary Text (550):
The invention also relates to a process for the preparation of crosslinked polymers by metathesis polymerization, wherein a composition of

Brief Summary Text (551):
(a) a catalytic amount of a one-component catalyst for metathesis polymerization and

Brief Summary Text (561):
In the case of irradiation using photoactive catalysts, the process according to the invention is preferably carried out at room temperature to slightly elevated temperature. An increase in temperature in this case essentially serves to increase the rate of reaction. At the temperatures chosen to accelerate the reaction, a photopolymerization therefore also chiefly takes place. However, it should be mentioned that the catalysts can be converted into thermoactive catalysts by adequate irradiation or elevated temperature. It is furthermore to be noted that some catalysts are capable of initiating the metathesis polymerization both thermally and [lacuna] irradiation.

Brief Summary Text (565):
The present invention also relates to crosslinked metathesis polymers of a polymer with strained cycloalkenylene radicals bonded in the polymer backbone, alone or as a mixture with strained cycloolefins.

Brief Summary Text (566):
The present invention also relates to metathesis polymers, crosslinked using a one-component catalyst, from a composition comprising

Brief Summary Text (567):
(a) a catalytic amount of a one-component catalyst for the metathesis polymerization and

Brief Summary Text (569):
Materials for production of shaped articles by machining, or shaped articles of all types directly, as well as coatings and relief images can be produced with the process according to the invention. The invention also relates to shaped articles of crosslinked metathesis polymers of the composition according to the invention.

Detailed Description Text (5):
55.1 g (0.5 mol) of Vestenamer.RTM. 6213 (cyclooctene polymerized by metathesis, Huls AG) are dissolved in 200 ml of toluene, the solution is mixed with 33.05 g (0.25 mol) of dicyclopentadiene and the mixture is heated at 190.degree. C. in an autoclave for 8 hours. During this operation, the dicyclopentadiene is cleaved to give cyclopentadiene, which reacts with the Vestenamer to form norbornene groups. The reaction mixture is then poured into methanol/acetone (1:1), while stirring, and the polymer which has precipitated out is filtered off and then dried. Yield 50.4 g (76%). Elemental analysis, % calculated (found): C 88.57 (88.38), H 11.43 (11.60).

Detailed Description Text (9):
55.1 g (0.5 mol) of Vestenamer.RTM. L3000 (cyclooctene of low molecular weight polymerized by metathesis, Huls AG, Marl) are mixed with 33.5 g (0.25 mol) of dicyclopentadiene without a solvent and the mixture is heated at 190.degree. C. in an autoclave for 8 hours. Working up and analysis of the reaction mixture are carried out analogously to Example A1. Yield 47.5 g (77%). Elemental analysis, % calculated (found): C, 88.57 (88.54), H, 11.43 (11.32). .sup.1 H-NMR analysis shows that 28% of the double bonds of the Vestenamer have been converted into norbornene units (x=0.28 and y=0.72). M.sub.n =500 g/mol; M.sub.w =5000 g/mol.

CLAIMS:

1. A composition comprising

(a) a catalytic amount of a one-component catalyst for metathesis polymerization, which one-component catalyst is selected from the group consisting of ruthenium and osmium compounds of the formulas XXV to XXVf

(R.sub.94 R.sub.95 R.sub.96 P)L.sub.8 Me.sup.2+ (Z.sup.1-).sub.2 (XXV)

(R.sub.94 R.sub.95 R.sub.96 P).sub.2 L.sub.9 Me.sup.2+ (Z.sup.1-).sub.2 (XXVa)

(R.sub.94 R.sub.95 R.sub.96 P)L.sub.9 L.sub.10 Me.sup.2+ (Z.sup.1-).sub.2 (XXVb)

(R.sub.94 R.sub.95 R.sub.96 P).sub.3 L.sub.9 Me.sup.2+ (Z.sup.1-).sub.2 (XXVc)

(R.sub.94 R.sub.95 R.sub.96 P)L.sub.9 L.sub.9 Me.sup.2+ (Z.sup.1-).sub.2 (XXVd)

(R.sub.94 R.sub.95 R.sub.96 P)L.sub.8 L.sub.10 Me.sup.2+ (Z.sup.1-).sub.2 (XXVe)

(R.sub.94 R.sub.95 R.sub.96 P)L.sub.8 (L.sub.9).sub.m Me.sup.2+ (Z.sup.1-).sub.2 (XXVf)

wherein

Me is Ru or Os;

Z in formulas XXV to XXVe is H.sup.-, cyclopentadienyl, Cl.sup.-, Br.sup.-, BF.sub.4.sup.-, PF.sub.6.sup.-, SbF.sub.6.sup.-, AsF.sub.6.sup.-, CF.sub.3 SO.sub.3.sup.-, C.sub.6 H.sub.5 --SO.sub.3.sup.-, 4-methyl-C.sub.6 H.sub.4 --SO.sub.3.sup.-, 3,5-dimethyl-C.sub.6 H.sub.3 --SO.sub.3.sup.-, 2,4,6-trimethyl-C.sub.6 H.sub.2 --SO.sub.3.sup.- and 4--CF.sub.3 --C.sub.6 H.sub.4 --SO.sub.3 --; or

Z in formula XXVf is H.sup.-, cyclopentadienyl, BF.sub.4.sup.-, PF.sub.6.sup.-, SbF.sub.6.sup.-, AsF.sub.6.sup.-, CF.sub.3 SO.sub.3.sup.-, C.sub.6 H.sub.5 --SO.sub.3.sup.-, 4-methyl-C.sub.6 H.sub.4 --SO.sub.3.sup.-, 3,5-dimethyl-C.sub.6 H.sub.3 --SO.sub.3.sup.-, 2,4,6-trimethyl-C.sub.6 H.sub.2 --SO.sub.3.sup.- and 4-CF.sub.3 --C.sub.6 H.sub.4 --SO.sub.3 --; or

R.sub.94, R.sub.95 and R.sub.96 independently of one another are C.sub.1 -C.sub.6 alkyl, or cyclopentyl or cyclohexyl or cyclopentyloxy or cyclohexyloxy which are unsubstituted or substituted by one to three C.sub.1 -C.sub.4 alkyl, or phenyl or benzyl or phenoxy or benzyloxy which are unsubstituted by one to three C.sub.1 -C.sub.4 alkyl;

L.sub.8 is C.sub.6 -C.sub.16 arene or C.sub.5 -C.sub.16 heteroarene which are unsubstituted or substituted by one to three C.sub.1 -C.sub.4 alkyl, C.sub.1 -C.sub.4 alkoxy, --OH, --F or --Cl;

L.sub.9 is C.sub.1 -C.sub.6 alkyl-CN, benzonitrile or benzylnitrile; and

L.sub.10 is H.sub.2 O or C.sub.1 -C.sub.6 alkanol; and

(b) at least one polymer with strained cycloalkenylene radicals bonded in the polymer backbone, alone or mixed with a strained cycloolefin.

10. A composition according to claim 1, wherein the polymers with a carbon backbone are metathesis polymers or copolymers of strained cycloolefins with a double bond in the ring and olefinically unsaturated comonomers, of which the olefinic double bonds in the polymer backbone are reacted partly or completely with open-chain or cyclic 1,3-dienes having 4 to 12 C atoms in a Diels-Alder reaction to give cycloalkenylene radicals having 6 to 14 C atoms.

12. A composition according to claim 10, wherein the metathesis polymers contain recurring structural elements of the formula (t) ##STR51##

in which A, is mono- or bicyclic C.sub.5 -C.sub.8 cycloalkenylene.

14. A composition according to claim 10, wherein the metathesis polymer contains recurring structural units of the formula (u) ##STR53##

and recurring structural elements of the formula (w)

--CH.dbd.CH--R.sub.026 -- (w),

in which A.sub.1, together with the --CH--CH--group, is bicyclic C.sub.5 -C.sub.8 cycloalkenylene and R.sub.026 is C.sub.1 -C.sub.12 alkylene, and, if desired, recurring structural elements of the formula (s) ##STR54##

in which R.sub.022 is H, F, C.sub.1 -C.sub.12 alkyl, --COOH, --C(O)O--C.sub.1 -C.sub.12 alkyl, --C(O)--NH.sub.2 or --C(O)--NH--C.sub.1 -C.sub.12 alkyl; R.sub.023 is H, F, Cl, CN or C.sub.1 -C.sub.12 alkyl; R.sub.024 is H, F, Cl, CN, OH, C.sub.1 -C.sub.12 alkyl, C.sub.1 -alkoxy, phenyl which is unsubstituted or substituted by

OH, Cl, Br, C.sub.1 -C.sub.4 alkyl, C.sub.1 -C.sub.4 alkoxy, --COOH, C(O)OC.sub.1 -C.sub.12 alkyl, --C(O)--NH.sub.2, --C(O)--NH--C.sub.1 -C.sub.12 alkyl, --SO.sub.3 H or --SO.sub.3 --C.sub.1 -C.sub.12 alkyl, --C(O)OH, --C(O)O--C.sub.2 --C.sub.12 hydroxyalkyl, --C(O)O--C.sub.1 -C.sub.12 alkyl, --C(O)--NH.sub.2 or --C(O)--NH--C.sub.1 -C.sub.12 alkyl; and R.sub.025 is H, F or C.sub.1 -C.sub.12 alkyl.

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